

acrolein with one mole of the divinyl ether also allows for the formation of a monomeric latent mercaptan of the mercaptan/tetrahydropyran adduct type in which the vinyl ether group of the resulting monomer permits the product to be copolymerized with one or more of a wide variety of ethylenically unsaturated compounds to form polymeric latent mercaptans. The product from the reaction of acrolein with chloroethyl vinyl ether provides a substituted 3,4-dihydropyran that can be further derivatized. The addition of a mercaptan across the double bond of the pyran ring can be done in the presence of one or more of the zinc salts to yield a stabilizer composition of this invention. Compounds having labile halogen atoms which split off as hydrogen chloride in a condensation reaction with the mercaptan, as exemplified by triphenylmethyl chloride, benzyl chloride, and bis(chloromethyl)benzene, are also suitable. The mercaptan may also be blocked by condensation with an aldehyde such as butyraldehyde or with a benzyl alcohol such as benzene dimethanol. The preferred blocking agents include the 3,4-dihydropyran (DHP) and 2-hydroxybenzyl alcohol, a well known intermediate in the perfume, agricultural, and plastics industries.

In general, the procedure for making latent mercaptans that are useful in this invention comprises adding the mercapto group of the free mercaptan across the double bonds of polarized, unsaturated compounds is as follows:

To a stirred mixture, under nitrogen atmosphere, of the mercaptan, acid catalyst, and optionally, a small percentage of antioxidant to inhibit radical reactions, is added dropwise to the polarized, unsaturated compound, either neat or in solution, while maintaining the temperature between 10-70°C.

The mixture or solution is then heated for between 1 and 6 hours at 35-70°C and conversion to product is monitored by gas chromatography and iodine titration for SH. The acid catalyst is removed by an alkaline wash and the resulting product is dried with magnesium sulfate and filtered. The solvent, if required, is removed under reduced pressure at <50°C to yield the latent mercaptan. A solid phase catalyst may be used and then filtered out of the reaction mixture and regenerated for use in a subsequent synthesis. In this way, a wash step is eliminated. This generalized procedure is referred to hereinafter as Procedure A.

In accordance with Procedure A, for example, mercaptoethanol is added across the double bond of N-vinylcaprolactam to yield N-2-hydroxyethylthioethylcaprolactam. Mercaptoethyldecanoate (mercaptoethylcaproate) reacts with 3,4-dihydropyran in that procedure to give 2-S-(tetrahydropyranyl)thioethyldecanoate. Bis(hydroxyethylthioethyl) cyclohexyl ether is made from the mercaptoethanol and cyclohexyl di-vinyl ether. In like manner, the corresponding caprate, oleate, and tallate esters form the corresponding cyclohexyl ethers. Also, indene is converted by the addition of the mercaptoethanol to 2H-dihydroindenylthioethanol. A generalized procedure for the condensation of a free mercaptan with a labile halogen-containing compound is as follows:

To a stirred mixture of the mercaptan and halogen-containing compound under nitrogen atmosphere is added dropwise a solution of sodium methoxide in methanol while maintaining the temperature below 50° C. Optionally, the reaction is allowed to proceed without the addition of a base source and the liberated hydrogen chloride is removed by

nitrogen gas sweep and neutralized with the use of an external acid scrubber. The mixture or solution is then heated for between 2 to 24 hours at 50°-70° C and conversion to product is monitored by gas chromatography and iodine titration for %SH. The product is then neutralized, washed with water, dried with magnesium sulfate, and filtered. The solvent, if required, is removed under reduced pressure at <50° C to yield the latent mercaptan. This generalized procedure is referred to hereinafter as Procedure B.

A generalized procedure for the condensation of a free mercaptan with a labile hydroxyl-containing compound is as follows:

To a stirred solution of the mercaptan, acid catalyst, and solvent under nitrogen atmosphere is added the hydroxy-containing compound either neat or in solution while maintaining the temperature <45° C. The solution is then heated to 45°-75° C for between 1 to 10 hours and conversion to product is monitored by gas chromatography and iodine titration for %SH. Optionally, an azeotropic solvent is chosen for removal of reaction water by an appropriate means at reflux temperatures, typically 60°-120° C. Completion of reaction is achieved after the theory amount of water has been collected. The acid catalyst is removed by alkaline wash and the resulting solution is dried with magnesium sulfate and filtered. The solvent is removed under reduced pressure at <55° C to yield the latent mercaptan. This procedure is referred to hereinafter as Procedure C.

For example, 2-hydroxybenzyl alcohol condenses with mercaptoethanol in accordance with Procedure C to form 1-(2-hydroxyphenyl)-1-S-(2-hydroxyethylthio)methane.